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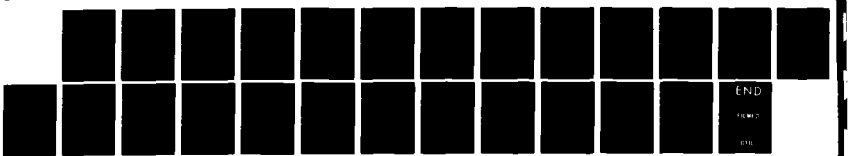

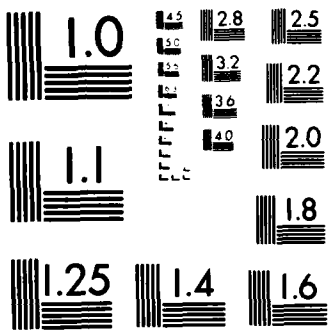

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Structures of Three Pyrazaboles: 1,3,5,7-Tetramethylpyrazabole; 4,4-Bis(pyrazol-1′-yl)pyrazabole; 4,4,8,8-Tetrakis(pyrazol-1′-yl)pyrazabole

by

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The structures of three pyrazaboles have been determined by single crystal x-ray diffraction. 1,3,5,7-Tetramethylpyrazabole: M_r = 215.9, monoclinic, $P2_1/c$, a = 7.552(1), b = 12.047(4), c = 13.814(6) Å, β = 91.27(2)°, V = 1256.5(7) Å^3 at T = 295 K, Z = 4, D_x = 1.141 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, u

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= 0.65 cm^{-1}, F(000) = 464, final R of 0.055 for 199 variables and 1640 reflections. 4,4-Bis(pyrazol-1′-yl)pyrazabole: M_r = 291.9, triclinic, $P\bar{1}$, a = 8.721(2), b = 9.351(2), c = 9.407(2) Å, α = 93.75(2), β = 100.75(2), γ = 92.73(2)°, V = 750.7(2) $Å^3$ at T = 295 K, Z = 2, D_x = 1.291 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, μ = 0.79 cm^{-1}, F(000) = 304, final R of 0.035 for 255 variables and 1957 reflections. 4,4,8,8-Tetrakis(pyrazol-1′-yl)pyrazabole: M_r = 424.0, monoclinic, $P2_1/n$, a = 8.849(2), b = 21.765(2), c = 11.672(1) Å, β = 109.51(1)°, V = 2118.9(5) $Å^3$ at 296 K, Z = 4, D_x = 1.329 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, μ = 0.82 cm^{-1}, F(000) = 880, final R of 0.036 for 362 variables and 1880 reflections. In all three structures the pyrazabole ring adopts a pronounced boat conformation. A comparison with the nine other known pyrazabole structures, however, shows that the central B_2N_2 ring is quite flexible, and that its observed conformation is sensitive to substituent and packing effects.

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Structures of Three Pyrazaboles: 1,3,5,7-Tetramethylpyrazabole ($C_{10}H_{18}B_2N_4$); 4,4-Bis(pyrazol-1′-yl)pyrazabole ($C_{12}H_{14}B_2N_8$); and 4,4,8,8-Tetrakis(pyrazol-1′-yl)pyrazabole ($C_{18}H_{18}B_2N_{12}$).

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Abstract. 1,3,5,7-Tetramethylpyrazabole (hereafter, ME4PZB): M_r = 215.9, monoclinic, $P2_1/c$, a = 7.552(1), b = 12.047(4), c = 13.814(6) Å, β = 91.27(2)°, V = 1256.5(7) Å^3 at T = 295 K, Z = 4, D_x = 1.141 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, μ = 0.65 cm^{-1}, $F(000)$ = 464, final R of 0.055 for 199 variables and 1424 reflections. 4,4-Bis(pyrazol-1′-yl)-pyrazabole (hereafter, BISPZB): M_r = 291.9, triclinic, $P\bar{1}$, a = 8.721(2), b = 9.351(2), c = 9.407(2) Å, α = 93.75(2), β = 100.75(2), γ = 92.73(2)°, V = 750.7(2) Å^3 at T = 295 K, Z = 2, D_x = 1.291 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, μ = 0.79 cm^{-1}, $F(000)$ = 304, final R of 0.035 for 255 variables and 1957 reflections. 4,4,8,8-Tetrakis(pyrazol-1′-yl)-pyrazabole (hereafter, TETPZB): M_r = 424.0, monoclinic, $P2_1/n$, a = 8.849(2),

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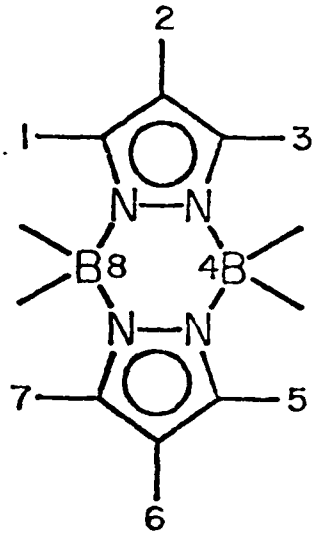
$\underline{b}$ = 21.765(2), $\underline{c}$ = 11.672(1) Å, $\underline{\beta}$ = 109.51(1)°, $\underline{V}$ = 2118.9(5) Å^3 at 296 K, Z = 4, D_x = 1.329 g cm^{-3}, MoKα, graphite monochromator, λ = 0.71069 Å, $\underline{\mu}$ = 0.82 cm^{-1}, $\underline{F}$(000) = 880, final $\underline{R}$ of 0.036 for 362 variables and 1880 reflections. In all three structures the pyrazabole adopts a pronounced boat conformation. A comparison with the nine other known pyrazabole structures, however, shows that the central B_2N_4 ring is quite flexible, and that its observed conformation is sensitive to substituent and packing effects.

Introduction. The pyrazaboles, which have the general structure and numbering scheme shown below, are a class of heterocycles containing four-coordinate boron and exhibiting remarkable chemical and thermal stability. Recent



efforts by one of us to exploit this stability (Clarke, Niedenzu, Niedenzu & Trofimenko, 1984) have focussed on synthesizing polymeric pyrazaboles containing boron atoms as spiro centers. In such a polymer the B_2N_4 ring must be approximately planar; however, if an analogy is made with 9,10-dihydroanthracene, the pyrazabole skeleton might just as well be expected to adopt a boat conformation (for discussion of the potential energy surface of 9,10-dihydroanthracene see Rabideau, 1978; Lipkowitz, Rabideau, Raber, Hardee, Schleyer, Kos & Kahn, 1982). The three structures reported here were undertaken in order to increase the information available about the pyrazabole ring system and its conformational flexibility.

Experimental. The structures of ME4PZ3 and BISPZB were determined at the University of Munich using a Syntex P3 diffractometer and the SHELXTL program

package. Crystals of ME4PZB (Trofimenko, 1967a) grown from CH_2Cl_2 as plates having faces of the forms {100}, {010}, and {001}. (Needles are obtained from toluene). Crystal 0.3 x 0.2 x 0.5 mm, ω-2θ scans, $2\theta \leq 45^{\circ}$, 3785 reflections (2 quadrants), after averaging 1424 with $F^2 > 3\sigma(F^2)$ treated as observed, 2 standard reflections, no absorption correction, decomposition (corrected) less than 2% overall, 21 reflections for measuring lattice parameters; $-8 \leq h \leq 8$, $k \leq 12$, $-14 \leq \ell \leq 14$. All C, B, and N atoms refined anisotropically; H atoms refined with fixed isotropic U's of 0.070 $\AA^2$. There was some difficulty in refining the methyl H atoms. Final values of agreement indices [refinement on F, $w^{-1} = \sigma^2(F_o) + (0.04\ F_o)^2$] are R = 0.055, wR = 0.055 for 199 variables; error in an observation of unit weight is 1.94; most important features in a final difference-Fourier map have heights +0.17 and -0.19 $e^-\ \AA^{-3}$. Positional parameters given in Table 1 and some bond lengths and angles in Tables 2 and 3; the molecular structure is illustrated in Figure 1. Crystals of BISPZB (Niedenzu & Niedenzu, 1984) grown from $CHCl_3/C_6H_{12}$ as prisms. Crystal 0.2 x 0.3 x 0.25 mm, ω-2θ scans, $2\theta \leq 45^{\circ}$, 4226 reflections (full sphere), after averaging 1957 with $F^2 > 3\sigma(F^2)$ treated as observed, 2 standard reflections, no absorption correction, decomposition (corrected) less than 1.8% overall, 14 reflections for measuring lattice parameters, $-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $\ell \leq 10$. All C, B, and N atoms refined anisotropically; H atoms refined isotropically. Final values of agreement indices [refinement on F, $w^{-1} = \sigma^2(F_o) + (0.02\ F_o)^2$] are R = 0.035, wR = 0.037 for 255 variables; error in an observation of unit weight is 1.89; most important features in a final difference-Fourier map have heights +0.09 and -0.21 $e^-\ \AA^{-3}$. Positional parameters given in Table 4 and some bond lengths and angles in Tables 2 and 3; the molecular structure is illustrated in Figure 2.

The structure of TETPZB was determined at the University of Kentucky using an Enraf-Nonius CAD4/F diffractometer and a program package described previously (Brock & Webster, 1976). Crystals of TETPZB (Trofimenko, 1967b) grown from $CHCl_3/C_6H_{12}$ as prisms elongated along a and bounded by faces of the forms {010}, {011}, and {10$\bar{1}$}. Crystal 0.15 x 0.22 x 0.38 mm (all thicker crystals examined were twinned), θ-2θ scans, $2\theta \leq 55^\circ$, 4839 reflections, 1880 with $F^2 > 2\sigma(F^2)$ treated as observed, 3 standard reflections, no absorption correction, correction for decomposition of 1.7% overall, 24 reflections having $22 < 2\theta < 24^\circ$ for measuring lattice parameters; $0 \leq h \leq 11$, $0 \leq k \leq 28$, $-15 \leq l \leq 15$. All C, B, and N atoms refined anisotropically, H atoms isotropically; an extinction factor (Zachariasen, 1967), final value 2.76(11) x 10^{-5}, improved agreement significantly. Final agreement indices [refinement on F, $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2)$ includes a term $(.02\ F_o^2)^2$] are R = 0.036, wR = 0.033 for 362 variables; error in an observation of unit weight is 1.38; most important features in a final difference-Fourier map have heights $\pm$0.17 e^- Å^{-3}. Positional parameters given in Table 5 and some bond lengths and angles in Tables 2 and 3; the molecular structure is illustrated in Figure 3.

Refined atomic displacement parameters and observed and calculated structure-factor amplitudes are available for all three structures.*

Discussion. If an analogy is made with 9,10-dihydroanthracene, the six-membered B_2N_4 ring of the pyrazabole would be expected to adopt either a boat or a planar conformation; however, the first structure of a member of this class [1,3,5,7,-tetramethyl-4,8-bis(3,5-dimethylpyrazol-1′-yl)pyrazabole;

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*The refined atomic displacement parameters and observed and calculated structure-factor amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP _____ (_____ pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Alcock & Sawyer, 1974] revealed a flattened chair conformation. The authors invoked steric interactions to explain this observation, and it is true that no other pyrazabole with comparable crowding has been studied crystallographically. The second structure done (2,6-dibromo-4,4,8,8-tetraethylpyrazabole; Holt, Tebben, Holt & Watson, 1977) contains a somewhat asymmetrical B_2N_4 ring that is approximately planar.

Quite recently ten more pyrazabole structures have been determined (Niedenzu & Nöth, 1983; Hanecker, Hodgkins, Niedenzu & Nöth, 1984; this work) and it is now possible to compare B_2N_4 ring conformations across a variety of substituents and crystal packing arrangements. Two dihedral angles have been chosen to describe ring geometries: an angle θ_1 between the plane of the four N atoms and a plane defined by a N-B-N grouping, and an angle θ_2 between the plane of the four N atoms and a bridging pyrazolyl ring. In the absence of imposed symmetry each molecule has two θ_1 and two θ_2 values, but in all cases but one (see below) the two corresponding values differ by at most a few degrees. The average value of the angle θ_1 measures the deviation of the B_2N_4 ring from planarity, and the average value of θ_2 describes the extent to which the bridging pyrazolyl rings are folded back in a butterfly arrangement. In all twelve structures the four N atoms of the B_2N_4 ring and the five atoms of the N_2C_3 rings form good planes; most deviations are much smaller than the maximum value of 0.02 Å.

A plot of θ_2 vs. θ_1 for eleven of the twelve structures (Figure 4) shows that a wide range of ring conformations has been observed. The interconversion of boat and chair forms must require only a small amount of energy, and must therefore be sensitive to substituent and packing effects. The boat form is, however, observed most frequently, and so is probably the

favored conformation.* The plot also confirms the expected correlation between θ_1 and θ_2: the more pronounced the boat conformation, the greater the bending back of the pyrazolyl rings. Evidence from molecular mechanics and quantum mechanical calculations for the related hydrocarbon 9,10-dihydroanthracene (Lipowitz et al., 1982) and from various studies of its derivatives (Rabideau, 1978) suggests that the energy difference between the boat and planar conformations in such ring systems is very small, perhaps less than 0.5 kcal/mol for a θ_2 value of 10 deg. In the pyrazaboles, which may be even more flexible than the hydrocarbon, the chair conformation is also accessible.

The one structure omitted from Figure 4 is that of 2,6-dibromo-4,4,8,8-tetraethylpyrazabole (Holt, Tebben, Holt & Watson, 1977). Its two angles θ_2 are similar at 1.2 and 3.2 deg, but the two values of θ_1, -0.5 and 12.2 deg, vary considerably. One end of the B_2N_4 ring is nearly planar, while the B atom at the other end is 0.24 Å out of the plane of the four N atoms. None of the other eleven structures even approaches this degree of asymmetry.

Differences in bond lengths and angles between bridging and terminal pyrazolyl rings are best examined in the structure of TETPZB. Not only is extensive averaging possible over the chemically equivalent bonds, but the internal consistancy of the four (or in two cases, two) independent length and angle determinations is excellent. Figure 5 shows some of the average values; bond angles in the B_2N_4 ring are in general sensitive to ring conformation and so are not included. There is clear evidence of localization of double bonds in the terminal rings. Although the differences within the pairs of N-C and C-C average bond lengths are small, they bracket the corresponding average

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*The recently completed structure of 4,4,8,8-tetrafluoropyrazabole (Nöth & Hanecker, 1984) also contains boat-shaped molecules with $\theta_1 = 30^\circ$.

values for the bridging rings. The same is true for the bond angles. Although a correction for the effects of thermal motion might increase the absolute values of these averages by ca. 0.003-0.006 Å, the pattern shown is probably insensitive to that kind of systematic error. A very similar pattern is also seen in the structure of BISPZ3. The structures of BISPZB and TETPZB show that a B-N bond to a terminal ring is about 0.040(4) Å shorter than a B-N bond to a bridging ring.

The B_2N_4 rings in both BISPZB and TETPZB adopt pronounced boat conformations (see Fig. 4); the arrangements of the two terminal rings on each B atom are also very similar (see Figs. 2 and 3). The orientations of the terminal rings in 4,8-diphenyl-4,8-bis(pyrazol-1′-yl)pyrazabole (Niedenzu & Nöth, 1983; site symmetry $\bar{1}$) are also related to those of BISPZB and TETPZB. The planes of the equatorial phenyl rings are almost perpendicular to the plane of the four N atoms and approximately bisect the N-B-N angles. The planes of the axial pyrazolyl rings are about perpendicular to both the equatorial rings and the central N-atom plane. The appearance of this same general arrangement of the terminal rings across three structures, two boat forms and one chair, suggests that it is the favored conformation for cis disubstitution by aromatic rings. In both BISPZB and TETPZB the uncoordinated N atoms of the pseudo-equatorial pyrazolyl rings are oriented so that the N-N bonds approximately eclipse the B-B vectors.

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References

ALCOCK, N.W. & SAWYER, J.F. (1974). Acta Cryst. B30, 2899-2901.

BROCK, C.P. & WEBSTER, D.F. (1976). Acta Cryst. B32, 2089-2094.

CLARKE, C.M., NIEDENZU, K., NIEDENZU, P.M. & TROFIMENKO, S. (1984). In Preparation.

HANECKER, E., HODGKINS, T.G., NIEDENZU, K. & NÖTH, H. (1984). Inorg. Chem., in press.

HOLT, E.M., TEBBEN, S.L., HOLT, S.L. & WATSON, K.J. (1977). Acta Cryst. B33, 1986-1988.

LIPKOWITZ, K.B., RABIDEAU, P.W., RABER, D.J., HARDEE, L.E., SCHLEYER, P.v.R., KOS, A.J. & KAHN, R.A. (1982). J. Org. Chem. 47, 1002-1005.

NIEDENZU, K. & NIEDENZU, P.M. (1984). Inorg. Chem., in press.

NIEDENZU, K. & NÖTH, H. (1983). Chem. Ber. 116, 1132-1153.

NÖTH, H. & HANECKER, E. (1984). In preparation.

RABIDEAU, P.W. (1978). Acc. Chem. Res. 11, 141-147.

TROFIMENKO, S. (1967a). J. Amer. Chem. Soc. 89, 3165-3170.

TROFIMENKO, S. (1967b). J. Amer. Chem. Soc. 89, 4948-4952.

ZACHARIASEN, W.H. (1967). Acta Cryst. 23, 558-564.

Table 1. Atom Coordinates (x 10^4) and Temperature Factors for 1,3,5,7-Tetramethylpyrazabole (ME4PZB)

Atom	x	y	z	B_{eq}, $Å^2$
B(1)	256(4)	898(3)	7196(2)	4.2
B(2)	-857(4)	2778(3)	6045(2)	4.1
N(1)	1682(2)	1732(2)	6842(1)	3.7
N(2)	1158(2)	2624(2)	6294(1)	3.8
N(3)	-1526(2)	1593(2)	5750(1)	3.5
N(4)	-999(2)	701(2)	6300(1)	3.4
C(1)	3451(3)	1783(2)	6971(2)	4.3
C(2)	4042(3)	2719(3)	6512(2)	5.1
C(3)	2594(3)	3232(2)	6086(2)	4.5
C(4)	-2569(3)	1228(2)	5016(2)	3.6
C(5)	-2705(3)	92(2)	5098(2)	3.7
C(6)	-1705(3)	-218(2)	5906(2)	3.4
C(11)	4454(5)	931(4)	7536(3)	6.3
C(31)	2458(4)	4266(3)	5505(3)	6.6
C(41)	-3364(4)	1983(3)	4275(2)	5.0
C(61)	-1416(4)	-1339(2)	6328(2)	4.7
H(11)	874(35)	133(20)	7446(18)	*
H(12)	-566(33)	1337(20)	7814(17)	*
H(21)	-1501(34)	3074(21)	6696(19)	*
H(22)	-995(34)	3322(21)	5444(19)	*
H(2)	5093(32)	2982(19)	6441(17)	*
H(5)	-3311(33)	-346(20)	4682(17)	*
H(11A)	5590(39)	1107(23)	7497(20)	*
H(11B)	4451(36)	197(25)	7228(19)	*
H(11C)	4229(38)	921(23)	8181(23)	*
H(31A)	3579(34)	4524(19)	5409(17)	*
H(31B)	1945(33)	4145(20)	4852(18)	*
H(31C)	1793(33)	4840(21)	5795(18)	*
H(41A)	-3870(37)	1612(22)	3769(21)	*
H(41B)	-2656(36)	2595(22)	4089(20)	*
H(41C)	-4339(33)	2381(21)	4512(18)	*
H(61A)	-2213(38)	-1494(23)	6785(21)	*
H(61B)	-346(37)	-1444(22)	6619(20)	*
H(61C)	-1593(36)	-1870(22)	5898(21)	*

*Fixed at 5.5 $Å^2$.

Table 2. Selected Bond Lengths (Å).

	ME4PZB	BISPZB	TETPZB
B(1)-N(1)	1.560(4)	1.549(2)	1.545(3)
B(1)-N(4)	1.561(3)	1.558(2)	1.551(3)
B(2)-N(2)	1.563(4)	1.563(2)	1.555(3)
B(2)-N(3)	1.566(4)	1.564(2)	1.557(3)
B(1)-N(5)		1.515(2)	1.516(3)
B(1)-N(7)		1.519(2)	1.510(3)
B(2)-N(9)			1.513(3)
B(2)-N(11)			1.519(3)
N(1)-N(2)	1.368(3)	1.368(1)	1.370(2)
N(3)-N(4)	1.369(3)	1.358(1)	1.369(2)
N(5)-N(6)		1.373(2)	1.367(3)
N(7)-N(8)		1.368(1)	1.364(3)
N(9)-N(10)			1.362(3)
N(11)-N(12)			1.372(3)
N(1)-C(1)	1.345(3)	1.346(2)	1.340(3)
N(2)-C(3)	1.345(3)	1.335(2)	1.342(3)
N(3)-C(4)	1.344(3)	1.336(2)	1.337(3)
N(4)-C(6)	1.339(3)	1.342(2)	1.331(3)
N(5)-C(7)		1.355(2)	1.356(3)
N(7)-C(10)		1.357(2)	1.354(3)
N(9)-C(13)			1.349(3)
N(11)-C(16)			1.351(3)
N(6)-C(9)		1.322(2)	1.326(3)
N(8)-C(12)		1.331(2)	1.324(3)
N(10)-C(15)			1.318(3)
N(12)-C(18)			1.338(4)
C(1)-C(2)	1.373(4)	1.370(2)	1.361(4)
C(2)-C(3)	1.377(4)	1.369(2)	1.360(4)
C(4)-C(5)	1.378(4)	1.372(2)	1.367(4)
C(5)-C(6)	1.385(4)	1.364(2)	1.364(4)
C(1)-C(11)	1.486(5)		
C(3)-C(31)	1.488(4)		
C(4)-C(41)	1.486(4)		
C(6)-C(61)	1.485(4)		
C(7)-C(8)		1.358(2)	1.358(4)
C(10)-C(11)		1.362(2)	1.352(5)
C(13)-C(14)			1.359(4)
C(16)-C(17)			1.362(4)
C(8)-C(9)		1.385(2)	1.379(4)
C(11)-C(12)		1.382(2)	1.370(5)
C(14)-C(15)			1.367(4)
C(17)-C(18)			1.364(5)
B(1)-H(11)	1.086(25)		
B(1)-H(12)	1.190(24)		
B(2)-H(21)	1.091(27)	1.151(13)	
B(2)-H(22)	1.061(26)	1.067(13)	

Table 3. Selected Bond Angles (°).

	ME4PZB	BISPZB	TETPZB
N(1)-B(1)-N(4)	105.1(2)	105.6(1)	105.6(2)
N(2)-B(2)-N(3)	104.8(2)	103.6(1)	105.3(2)
N(1)-B(1)-N(5)		111.2(1)	109.4(2)
N(4)-B(1)-N(5)		109.2(1)	110.8(2)
N(1)-B(1)-N(7)		109.7(1)	110.7(2)
N(4)-B(1)-N(7)		110.5(1)	110.0(2)
N(2)-B(2)-N(9)			109.3(2)
N(3)-B(2)-N(9)			109.6(2)
N(2)-B(2)-N(11)			110.9(2)
N(3)-B(2)-N(11)			109.5(2)
N(5)-B(1)-N(7)		110.5(1)	110.2(2)
N(9)-B(2)-N(11)			112.0(2)
B(1)-N(1)-N(2)	119.1(2)	119.6(1)	121.2(2)
B(1)-N(4)-N(3)	118.9(2)	121.0(1)	121.6(2)
B(2)-N(2)-N(1)	118.9(2)	121.0(1)	122.3(2)
B(2)-N(3)-N(4)	118.9(2)	119.7(1)	121.9(2)
H(11)-B(1)-H(12)	112.1(18)		
H(21)-B(2)-H(22)	113.9(19)	115.7(10)	

Table 4. Atom Coordinates (x 10^4) and Temperature Factors for 4,4-Bis(pyrazol-1′-yl)pyrazabole (BISPZB).

Atom	x	y	z	B_{eq} or B, $Å^2$
B(1)	6515(2)	2269(2)	7138(2)	3.2
B(2)	8782(2)	4539(2)	6679(2)	4.4
N(1)	6286(1)	2975(1)	5674(1)	3.5
N(2)	7339(1)	4037(1)	5466(1)	3.8
N(3)	8094(1)	4599(1)	8101(1)	3.9
N(4)	7094(1)	3515(1)	8327(1)	3.5
N(5)	4988(1)	1586(1)	7392(1)	3.5
N(6)	3642(1)	3213(1)	7231(1)	4.4
N(7)	7734(1)	1159(1)	7163(1)	3.5
N(8)	8486(1)	0723(1)	8457(1)	4.4
C(1)	5161(2)	2788(2)	4474(1)	4.2
C(2)	5498(2)	3720(2)	3494(2)	4.9
C(3)	6854(2)	4486(2)	4148(2)	4.7
C(4)	8290(2)	5548(2)	9254(2)	4.9
C(5)	7427(2)	5084(2)	10230(2)	5.4
C(6)	6690(2)	3812(2)	9618(2)	4.5
C(7)	4747(2)	0317(2)	7957(2)	4.3
C(8)	3248(2)	0210(2)	8165(2)	5.2
C(9)	2611(2)	1463(2)	7690(2)	4.5
C(10)	8005(2)	0272(1)	6048(2)	4.3
C(11)	8944(2)	-0753(2)	6619(2)	5.2
C(12)	9208(2)	-0432(2)	8103(2)	4.8
H(21)	9673(15)	3667(13)	6693(13)	4.3(3)
H(22)	9202(16)	5594(14)	6514(14)	5.2(3)
H(1)	4263(15)	2079(13)	4457(14)	4.8(3)
H(2)	4870(18)	3782(15)	2585(17)	5.4(3)
H(3)	7417(18)	5285(16)	3866(17)	6.5(4)
H(4)	8954(18)	6369(16)	9228(16)	6.2(3)
H(5)	7352(19)	5581(17)	11097(18)	7.2(4)
H(6)	5962(17)	3181(15)	9949(15)	4.8(3)
H(7)	5550(17)	-0298(14)	8136(14)	4.3(3)
H(8)	1553(17)	1736(15)	7655(15)	5.6(3)
H(9)	2738(19)	-0553(17)	8497(17)	6.3(4)
H(10)	7585(16)	0442(14)	5069(14)	5.2(3)
H(11)	9342(18)	-1445(15)	6086(16)	6.2(3)
H(12)	9857(18)	-0884(16)	8878(17)	5.9(3)

TABLE 5. POSITIONAL AND THERMAL PARAMETERS FOR THE ATOMS OF 4,4,8,8-TETRAKIS(PYRAZOL-1'-YL)PYRAZABOLE (TETPZB)

ATOM	X[A]	Y	Z	B or B_{eq}, $Å^2$[B]	ATOM	X	Y	Z	B or B_{eq}, $Å^2$[B]
N(1)	0.2693(2)	0.44465(9)	-0.08711(16)	2.9	C(14)	0.5864(5)	0.36251(16)	0.4061(3)	5.8
N(2)	0.3173(2)	0.43257(9)	0.03503(16)	2.9	C(15)	0.6871(4)	0.37568(15)	0.3426(3)	5.3
N(3)	0.3921(2)	0.32562(9)	-0.00359(17)	2.9	C(16)	0.0790(4)	0.29476(15)	0.0345(3)	4.1
N(4)	0.3342(2)	0.33808(9)	-0.12546(17)	3.1	C(17)	-0.0576(4)	0.29467(20)	0.0640(3)	5.4
N(5)	0.0471(2)	0.37466(10)	-0.20291(17)	3.3	C(18)	-0.0463(4)	0.3455(2)	0.1346(3)	5.7
N(6)	-0.0083(3)	0.31939(11)	-0.25603(19)	4.3	B(1)	0.2200(4)	0.39235(14)	-0.1818(3)	3.1
N(7)	0.2405(2)	0.41195(10)	-0.29988(17)	3.5	B(2)	0.3286(3)	0.36608(14)	0.0860(2)	3.1
N(8)	0.3874(3)	0.42733(11)	-0.30525(20)	4.6	H(1)	0.245(3)	0.5225(10)	-0.181(2)	3.9 (6)
N(9)	0.4552(2)	0.36386(9)	0.21086(16)	3.4	H(2)	0.327(3)	0.5733(12)	0.025(2)	3.6 (6)
N(10)	0.6107(3)	0.37695(11)	0.22437(19)	4.8	H(3)	0.383(3)	0.4855(10)	0.177(2)	3.8 (6)
N(11)	0.1664(2)	0.34424(10)	0.08784(17)	3.5	H(4)	0.512(3)	0.2598(10)	0.097(2)	3.6 (6)
N(12)	0.0891(3)	0.37726(12)	0.1518(2)	5.1	H(5)	0.540(3)	0.2223(12)	-0.100(2)	4.6 (7)
C(1)	0.2696(3)	0.50575(13)	-0.1012(3)	3.6	H(6)	0.378(3)	0.2960(11)	-0.266(2)	4.9 (6)
C(2)	0.3166(4)	0.53323(15)	0.0099(3)	4.1	H(7)	-0.053(3)	0.4488(13)	-0.152(2)	4.6 (7)
C(3)	0.3466(3)	0.48689(13)	0.0927(3)	3.6	H(8)	-0.315(4)	0.3888(13)	-0.235(3)	6.9 (9)
C(4)	0.4722(3)	0.27481(13)	0.0169(3)	3.7	H(9)	-0.226(3)	0.2846(12)	-0.304(2)	5.0 (7)
C(5)	0.4831(4)	0.25451(15)	-0.0909(3)	4.3	H(10)	0.019(4)	0.4114(15)	-0.416(3)	8.7 (11)
C(6)	0.3965(3)	0.29495(13)	-0.1772(3)	3.9	H(11)	0.150(4)	0.4413(17)	-0.577(3)	10.8 (11)
C(7)	-0.0746(4)	0.40801(16)	-0.1883(3)	4.1	H(12)	0.452(4)	0.4547(14)	-0.443(3)	7.1 (9)
C(8)	-0.2113(4)	0.37448(17)	-0.2319(3)	4.6	H(13)	0.337(3)	0.3473(12)	0.325(2)	5.6 (8)
C(9)	-0.1639(4)	0.32060(17)	-0.2720(3)	4.8	H(14)	0.613(4)	0.3581(14)	0.486(3)	7.5 (9)
C(10)	0.1277(5)	0.41810(19)	-0.4110(3)	6.2	H(15)	0.807(4)	0.3849(12)	0.370(2)	6.1 (8)
C(11)	0.2014(5)	0.4371(2)	-0.4892(3)	8.0	H(16)	0.113(3)	0.2681(13)	-0.020(2)	6.3 (8)
C(12)	0.3601(5)	0.44229(17)	-0.4203(3)	6.0	H(17)	-0.142(4)	0.2661(14)	0.034(3)	7.2 (9)
C(13)	0.4395(5)	0.35468(15)	0.3206(3)	4.9	H(18)	-0.117(4)	0.3630(13)	0.175(2)	6.8 (8)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES.

[B] THE EQUIVALENT B'S ARE CALCULATED FROM THE ANISOTROPIC THERMAL PARAMETERS FOR THE

Figure Captions

Figure 1. Perspective drawing of the molecular structure of 1,3,5,7-tetramethylpyrazabole (ME4PZB). In this and the following drawings the shapes of the ellipsoids for the non-H atoms correspond to 50% probability contours of atomic displacement.

Figure 2. Perspective drawing of the molecular structure of 4,4-bis(pyrazol-1′-yl)pyrazabole (BISPZB).

Figure 3. Perspective drawing of the molecular structure of 4,4,8,8-tetrakis(pyrazol-1′-yl)pyrazabole (TETPZB).

Figure 4. A scatter plot showing the relationship between the dihedral angles θ_1 of the planes (B1,N1,N4) and (B2,N2,N3) with the plane (N1,N2,N3,N4), and the angles θ_2 of the planes (N1,N2,C1,C2,C3) and (N3,N4,C4,C5,C6) with the plane (N1,N2,N3,N4) for 11 pyrazabole structures (see Fig. 1-3 for the atom-numbering scheme). The structures are (1) 1,3,5,7-tetramethyl-4,8-bis(3,5-dimethylpyrazol-1′-yl)pyrazabole (Alcock & Sawyer, 1974); (2) 4,4,8,8-bis(ethylenedithio)pyrazabole (Niedenzu & Nöth, 1983); (3) 4,4,8,8-tetrakis(methylthio)pyrazabole (Niedenzu & Nöth, 1983); (4) 4,4,8,8-tetrachloropyrazabole (Niedenzu & Nöth, 1983); (5) 4,8-diphenyl-4,8-bis(pyrazol-1′-yl)pyrazabole (Niedenzu & Nöth, 1983); (6) 4,8-dibromo-2,6-dichloropyrazabole (Niedenzu & Nöth, 1983); (7) pyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1984); (8) 4,4,8,8-tetrabromopyrazabole (Hanecker, Hodgkins, Niedenzu & Nöth, 1984); (9) 1,3,5,7-tetramethylpyrazabole (this paper); (10)

4,4-bis(pyrazol-1′-yl)pyrazabole (this paper); and (11) 4,4,8,8-tetrakis(pyrazol-1′-yl)pyrazabole (this paper). The rectangle for each structure covers the range of the two θ_1 and two θ_2 values that are observed in the absence of imposed symmetry (see text).

Figure 5. Diagram showing some average bond lengths and angles for 4,4,8,8-tetrakis(pyrazabol-1′-yl)pyrazabole. The numbers in parentheses are the esd′s of the means. The esd′s for the angles range from 0.1 to 0.4 deg, and average 0.2 deg.

Figure 1.

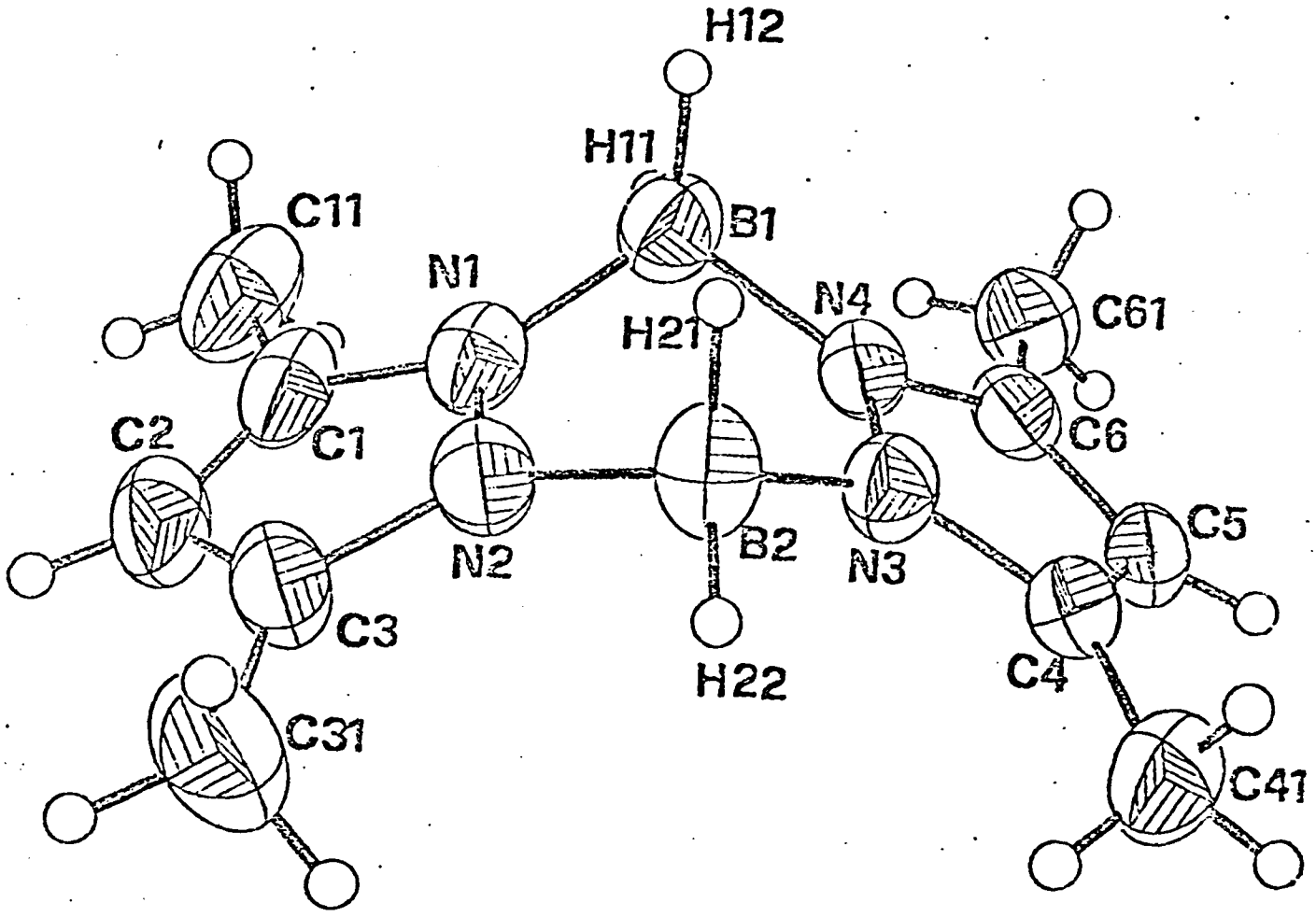
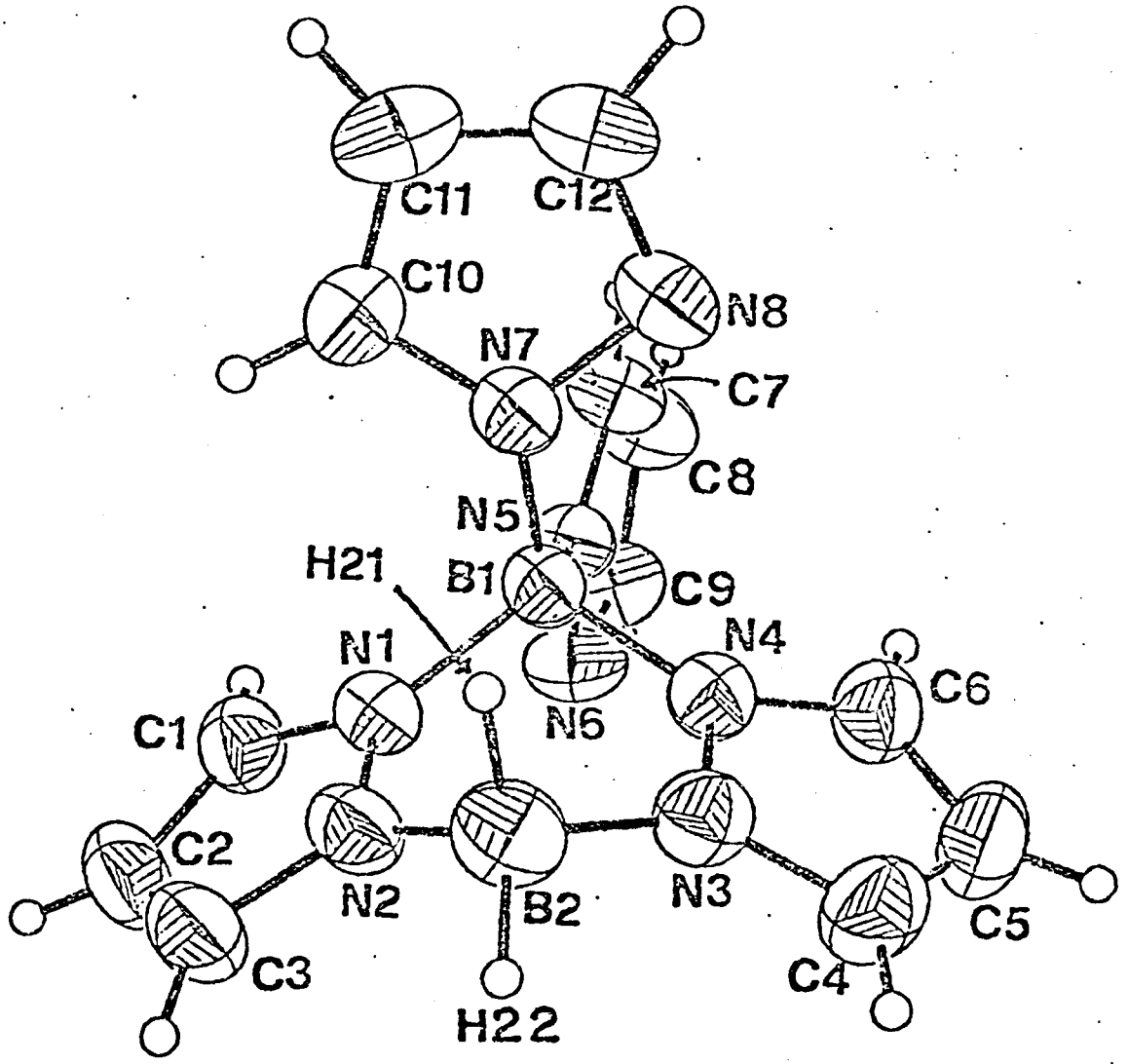


Figure 2.


C11
C12
C10
N8
N7
C7
C8
N5
H21
B1
C9
N1
N4
C6
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N6
C2
N2
B2
N3
C5
C3
C4
H22

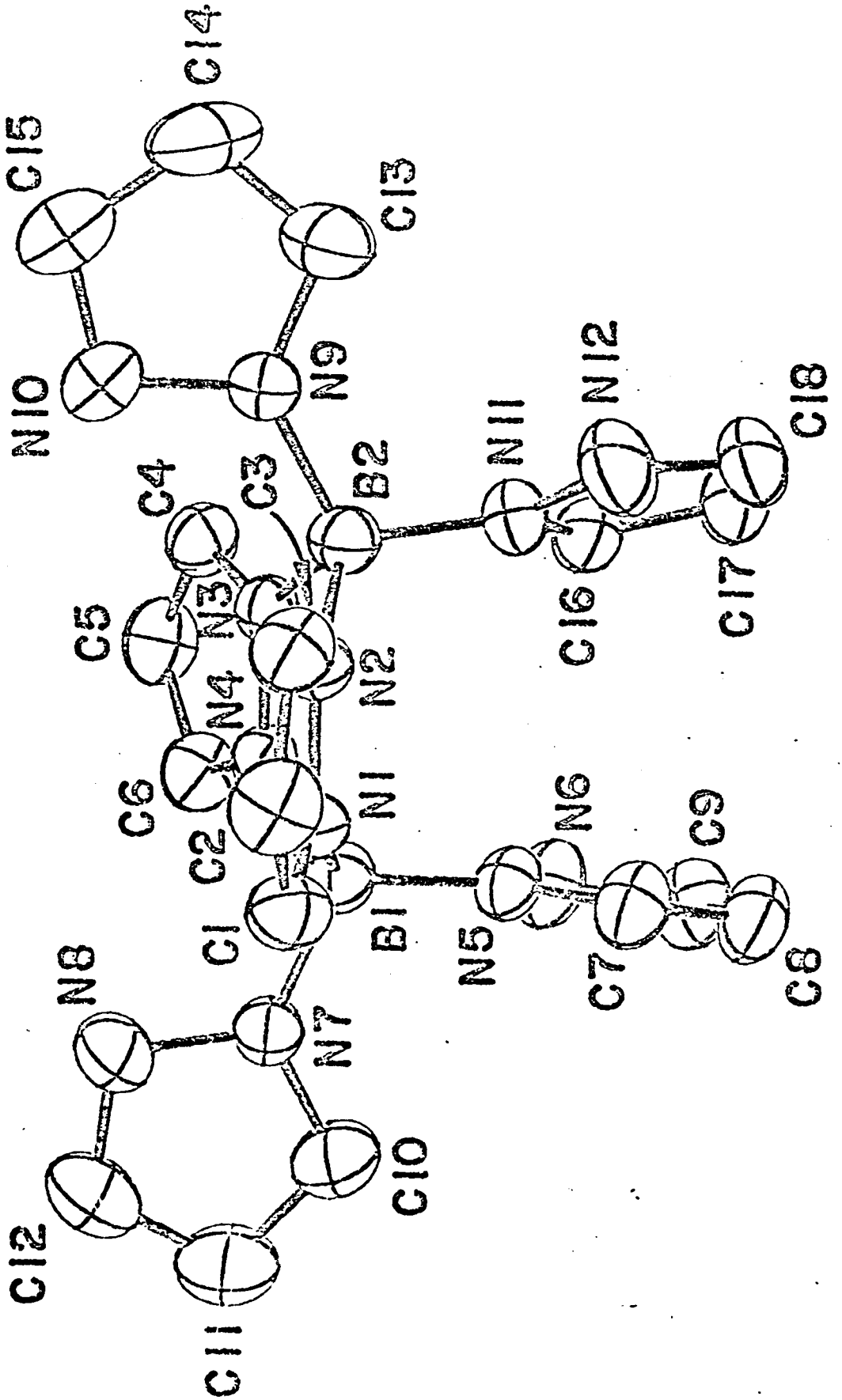

C14
C15
C13
N10
N9
N11
N12
C18
C4
C3
B2
C5
N3
C16
C17
N4
N2
C6
N1
N6
C9
C2
C1
B1
N5
C7
C8
N8
N7
C12
C10
C11

Figure 3.

Figure 4.

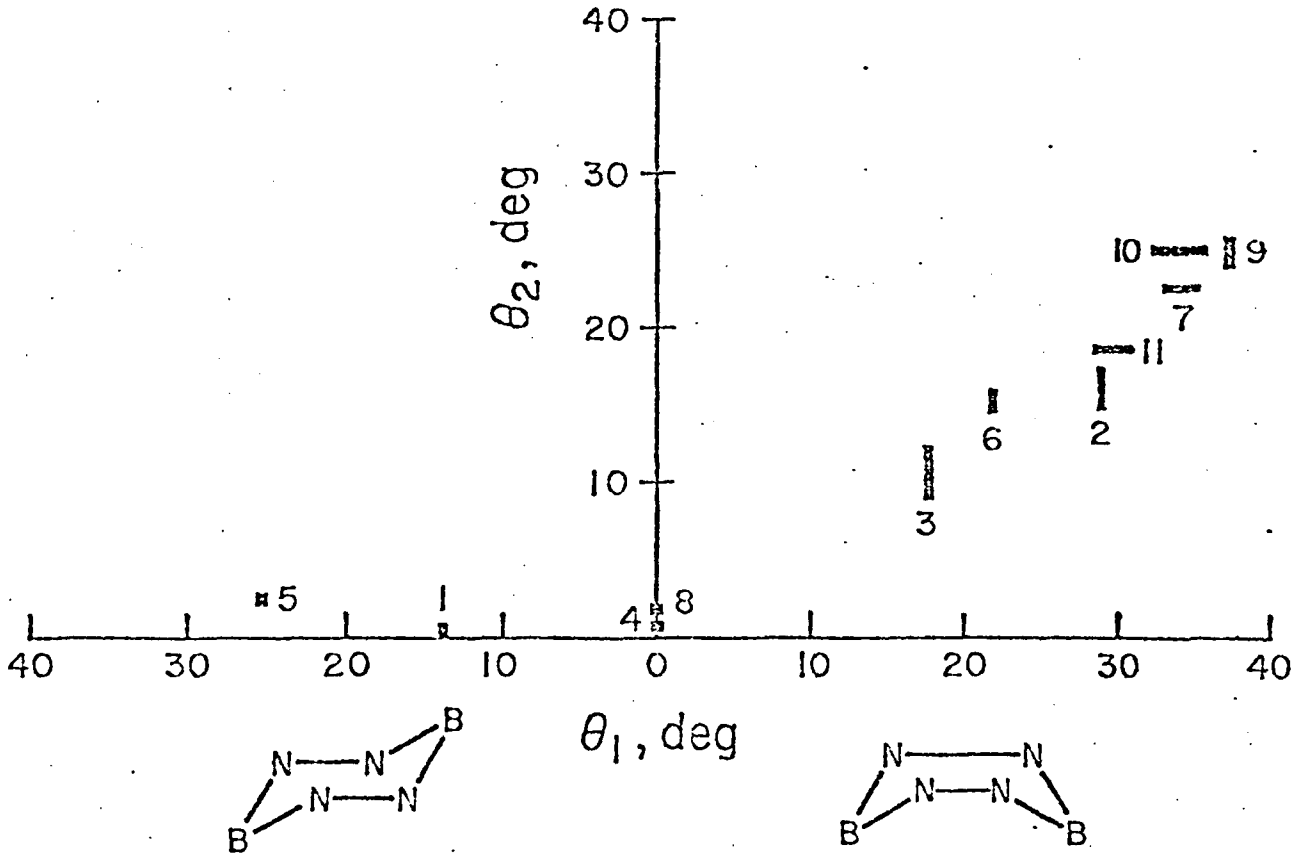
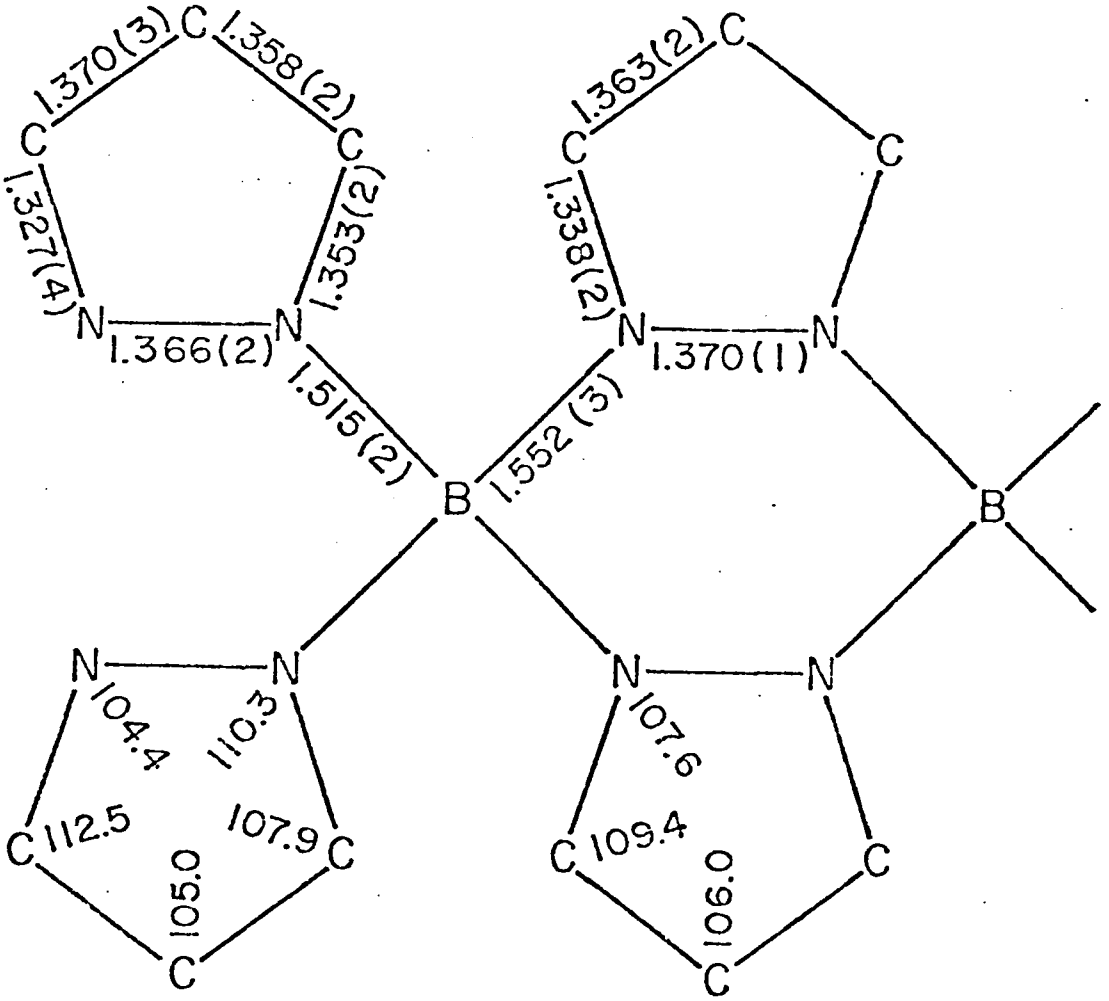

40
30
20
10
θ2, deg
10
9
7
11
6
2
3
5
1
4
8
40
30
20
10
0
10
20
30
40
θ1, deg
N
N
N
N
B
B
N
N
N
N
B
B

Figure 5.


1.370(3)
C
1.358(2)
C
C
1.327(4)
N
1.366(2)
N
1.353(2)
1.515(2)
B
1.552(3)
1.363(2)
C
C
C
1.338(2)
N
1.370(1)
N
B
N
N
104.4
110.3
C
112.5
107.9
C
105.0
C
N
N
107.6
C
109.4
C
109.0
C

END

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2-85

DTIC